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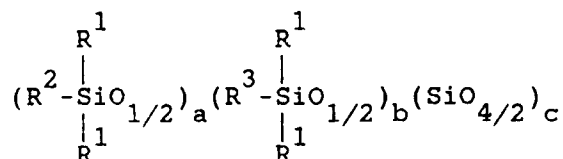
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D-80336 München (DE)**(54) **Curable silicone composition.**

(57) The present invention pertains to a curable silicone composition comprised of (A) an organopolysiloxane represented by the formula



wherein R¹ is a monovalent hydrocarbon group other than an alkenyl group; R² is a monovalent hydrocarbon group other than an alkenyl group or hydrogen; R³ is an organic group that contains an epoxy group or an alkoxyalkyl group with the proviso that at least one R³ group is an organic group containing an epoxy group; a is either 0 or a positive number; b is a positive number; c is a positive number; a/c has a value of between 0 to 4, b/c has a value of between 0.05 to 4, and (a + b)/c has a value of between 0.2 to 4; and (B) a curing compound selected from curing agents or curing catalysts.

The curable silicone composition of the present invention has superior curing properties and is capable of forming a hardened silicone material with superior flexibility and heat resistance after curing.

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Because of their superior adhesive properties, bonding properties, environmental resistance, and electrical properties after the silicone is hardened curable silicone compositions are used for electric and electronic fillers, adhesives for electric and electronic applications, coating compositions, and coating materials for rubber. Silicone compositions curable by a condensation-reaction which undergo curing by a dehydration-condensation reaction of silanol groups, dehydrogenation between a silanol group and a hydrogen bonded to a silicon atom, dealcohol reaction between a silanol group and silicon atom bonded alkoxy group, and silicone compositions curable by an adduct reaction which undergo curing by an adduct reaction between the silicon atom, hydrogen and fatty acid unsaturated groups in the presence of hydrosilylation reaction catalysts are known in the art.

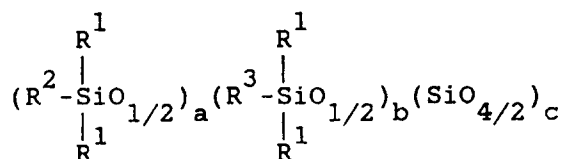
However, in the silicone compositions curable by a condensation reaction, the curing requires a very long time and the curing property is inferior; in the case of silicone compositions curable by an adduct reaction, curing does not progress in the presence of adduct reaction inhibitors such as sulfur and soldering flux, and the surface of the composition is less likely to be hardened because of oxygen. In addition, in general, the heat resistance of the curable silicone composition is inferior after curing.

For this reason, various types of curable silicone compositions with improved curing properties have been suggested. Curable silicone compositions comprised of a hydrolysate of an organic silane containing an epoxy group and ammonium perchlorate are disclosed in Japanese Kokai Patent Application No. Sho 56[1981]-72054 and curable silicone compositions comprised of an organopolysiloxane containing at least two epoxy groups in a single molecule, organopolysiloxane containing at least two amino groups in a single molecule, and an epoxy curing catalyst are disclosed in Japanese Kokai Patent Application No. Sho 60-[1985]-179417.

However, the curing properties of curable silicone compositions suggested in Japanese Kokai Patent Application No. Sho 56[1981]-72054 and Japanese Kokai Patent Application No. Sho 60[1985]-179417 are insufficient, and the flexibility and heat resistance of the cured silicone material are inferior.

It is an object of the present invention is to produce a curable silicone composition with superior curing properties that forms a hard silicone material with superior flexibility and heat resistance after curing.

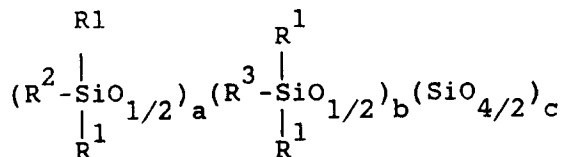
The present invention pertains to a curable silicone composition comprised of (A) an organopolysiloxane represented by the formula



wherein R¹ is a monovalent hydrocarbon group other than an alkenyl group; R² is a monovalent hydrocarbon group other than an alkenyl group or hydrogen; R³ is an organic group that contains an epoxy group or an alkoxysilylalkyl group with the proviso that at least one R³ group is an organic group containing an epoxy group; a is either 0 or a positive number; b is a positive number; c is a positive number; a/c has a value of between 0 to 4, b/c has a value of between 0.05 to 4, and (a + b)/c has a value of between 0.2 to 4; and (B) a curing compound selected from curing agents or curing catalysts.

The curable silicone composition of the instant invention is mainly comprised of an organopolysiloxane made of monofunctional siloxane units (M units) and quaternary functional siloxane units (Q units) and has superior curing properties that forms a hardened silicone material with superior flexibility and heat resistance after curing.

The organopolysiloxane, component (A), is the primary component of the present invention and is represented by the formula:



is less than 0.1 part by weight per 100 parts by weight of component (A), the curing reaction is less likely to be initiated, and when the amount exceeds 500 parts by weight, a sufficient degree of the curing reaction fails to occur.

In addition, the curable silicone composition of the present invention which is mainly composed of component (A) and component (B) may include fillers such as aerosol silica, crystalline silica, fused silica, wet silica, titanium oxide, zinc carbonate, calcium carbonate, iron oxide, and carbon black, fatty acid esters such as stearic acid ester, and palmitic acid ester, metal salts, ester-based waxes, and plasticizers.

The curable silicone composition of the present invention has superior curing properties and forms a hard silicone material with a superior flexibility and heat resistance after curing. Therefore, it can be used effectively for coating compositions, coating agents for electric and electronic parts, adhesives, sealers for electric and electronic parts, sealing agents for high temperature areas such as automobile engines, and for a composition that provides flexibility in the curable resin compositions.

So that those skilled in the art can understand and appreciate the invention taught herein, the following examples are presented.

In the following examples the value of the viscosity in application examples is the value measured at 25 °C, and curable silicone compositions were cured by heating at 150 °C for 3 hours. Furthermore, measurement of physical properties of the hardened silicone material was carried out as described below.

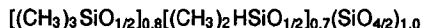
Heat resistance: A small piece of hardened silicone was heated in air at a rate of temperature increase of 10 °C/min by thermogravimetric analysis (TGA), and is shown as the residual (wt%) at 850 °C.

Flexibility: Both ends of a hardened silicone material molded to form a 1/4 x 1/2 x 4 inch (0.635 x 1.27 x 10.16 centimeter) bar were fixed, then a 5 kg weight was hung from the center of the hardened silicone material, and the warping at the center area was measured. When the warping was less than 0.5 cm, it is classified as x, when 0.5-1 cm, it is classified as Δ, and when it exceeds 1 cm, it is classified as O.

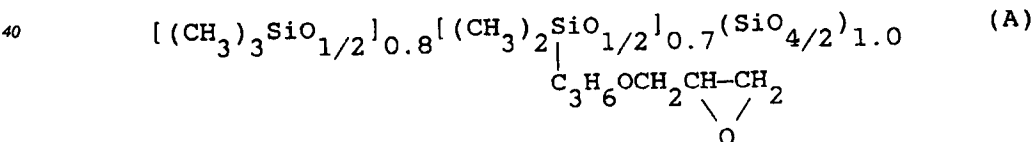
Hardness: A hardened silicone material molded to form a disc 2 inches (5.08 cm) in diameter x 1/10 inch (0.254 cm) was measured by a Barcol 935 hardness meter.

Preparation Example 1

An organopolysiloxane shown by the formula



(viscosity 105 centipoise (k Pa.s), silicon-bonded hydrogen content 0.40 wt%) was reacted with an excess amount of allyl glycidyl ether in toluene using chloroplatinate as a catalyst. An organopolysiloxane having the formula:



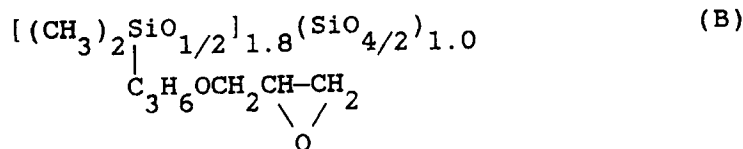
was produced. The viscosity of the organopolysiloxane produced was 520 centipoise (k Pa.s), and the epoxy equivalence was 420.

Preparation Example 2

An organopolysiloxane shown by the formula:



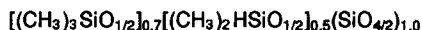
(viscosity 46 centipoise (k Pa.s), silicon-bonded hydrogen content 0.92 wt%) was reacted with an excess amount of allyl glycidyl ether in toluene with chloroplatinate as a catalyst. An organopolysiloxane having the formula:



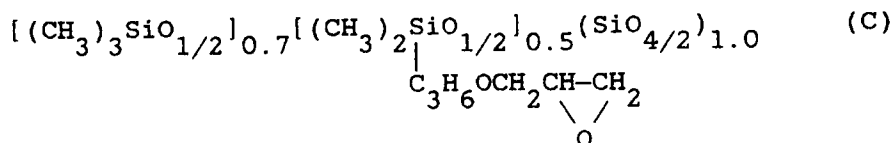
was produced. The viscosity of the organopolysiloxane produced was 610 centipoise (k Pa.s), and the epoxy equivalence was 370.

Preparation Example 3

A viscous organopolysiloxane shown by the formula



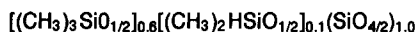
(silicon-bonded hydrogen content 0.33 wt%) was reacted in toluene with an excess amount of allyl glycidyl ether with chloroplatinate as a catalyst. An organopolysiloxane having the formula:



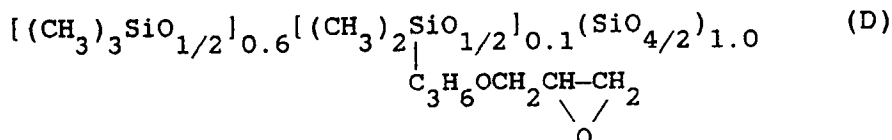
was produced. The organopolysiloxane produced had a semitransparent brown color, and the epoxy equivalence was 1100.

Preparation Example 4

An organopolysiloxane shown by the formula



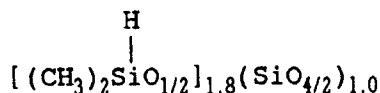
(silicon-bonded hydrogen content 0.09 wt%) was reacted in toluene with an excess amount of allyl glycidyl ether with chloroplatinate as a catalyst. An organopolysiloxane having the formula



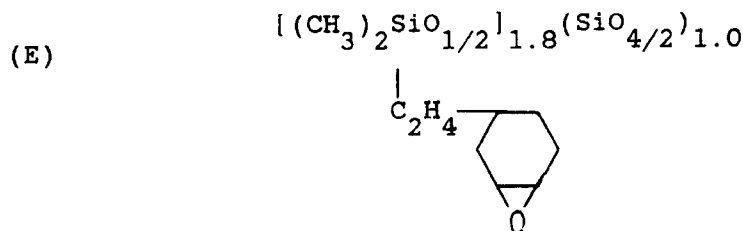
was produced. The organopolysiloxane produced had a semitransparent brown color, and the epoxy equivalence was 1290.

Preparation Example 5

An organopolysiloxane shown by the formula



(viscosity 46 centipoise (k Pa.s), silicon-bonded hydrogen content 0.92 wt%) was reacted in toluene with an excess amount of 1,2-epoxy-4-vinylcyclosiloxane with chloroplatinate as a catalyst. An organopolysiloxane having the formula



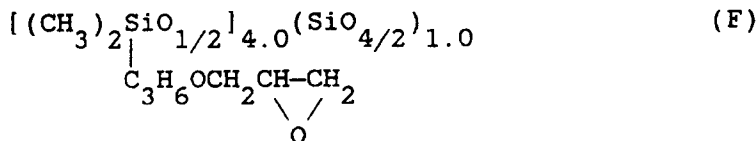
was produced. The organopolysiloxane produced had a semitransparent brown color, the viscosity was 520 centipoise (k Pa.s), and the epoxy equivalence was 230.

Preparation Example 6

An organopolysiloxane shown by the formula



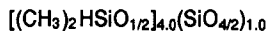
(boiling point 190°C, silicon-bonded hydrogen content 1.22 wt%) was reacted in toluene with an excess amount of allyl glycidyl ether with chloroplatinate as a catalyst, and organopolysiloxane having the formula:



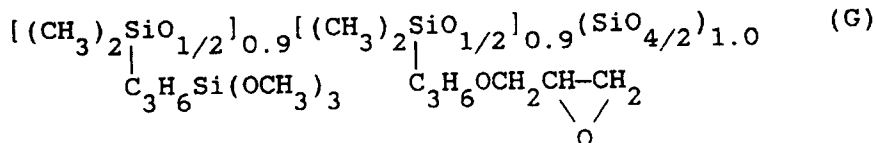
below was produced. The organopolysiloxane produced was a semitransparent brown color, the viscosity was 54 centipoise (k Pa.s), and the epoxy equivalence was 205.

Preparation Example 7

An organopolysiloxane shown by the formula



(viscosity 46 centipoise, silicon-bonded hydrogen content 0.92 wt%) was reacted in toluene with a mixture composed of allyl glycidyl ether and allyltrimethoxysilane = 1:1 with chloroplatinate as a catalyst. An organopolysiloxane having the formula



was produced. The organopolysiloxane produced had a semitransparent yellow color, and the viscosity was 200 centipoise (k Pa.s).

EXAMPLE 1

Organopolysiloxanes produced in the Preparation Examples, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 3- or 4-methylhexahydrophthalic anhydride, and 2,4,6-(trisdimethylaminomethyl)-phenol were uniformly mixed in the weight ratio listed in Table I, and curable silicone compositions were produced. These curable silicone compositions were cured, and the properties of the hardened silicone materials were evaluated. These results are shown in Table I.

Also, the hardness of the curable silicone composition mixed with the organopolysiloxane prepared in Preparation Example 2 after curing was 55.

COMPARATIVE EXAMPLE 1

The organopolysiloxane was omitted, and a curable epoxy resin composition was prepared in the weight ratio shown in Table I. The curable epoxy resin composition was cured as in Example 1, and physical properties of the hardened material were evaluated. Results are shown in Table I.

Also, the hardness of the hardened material was 55, and it was confirmed that no differences existed in the degree of hardness from the hardened material measured in Example 1.

Table I

Type of organopolysiloxane	Example 1						Comparative Example 1
	A	B	C/F	D/G	E	E	
Organopolysiloxane	100	100	95/5	95/5	100	50	--
A*	--	--	--	--	--	50	100
B*	37.6	42.7	14.4	12.2	40.5	76.6	120.5
C*	1	1	1	1	1	1	1
Flexibility	0	0	0	Δ	Δ	Δ	X
Residual (wt%)	33	25	55	63	27	11	0

*A: 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate

B: 3- or 4-Methylhexahydrophthalic anhydride

C: 2,4,6-(Trisdimethylaminomethyl)phenol

EXAMPLE 2

In addition to the components of Example 1, a fused silica with an average grain diameter of 13 μ m was added, and a curable silicone composition was produced as in Example 1. The curable silicone composition produced was cured as in Example 1, and the physical properties of the hardened silicone material were measured. Results are shown in Table II.

Table II

Type of organopolysiloxane	Example 2	
	E	E
Organopolysiloxane	100	50
A*	--	50
B*	40.5	76.6
Fused silica	137.5	169.9
C*	1	1
Flexibility	Δ	Δ
Residual (wt%)	65	57

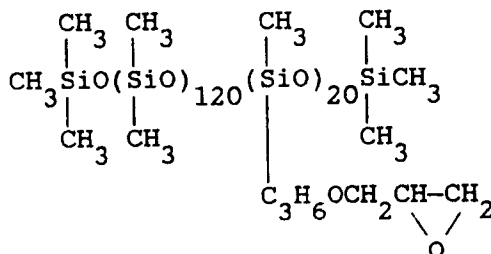
*A: 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate

B: 3- or 4-Methylhexahydrophthalic anhydride

C: 2,4,6-(Trisdimethylaminomethyl)phenol

COMPARATIVE EXAMPLE 2

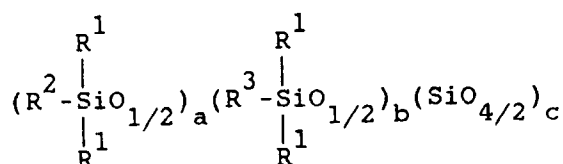
The same components as used in Example 1 were used except the organopolysiloxane shown in the following formula was used, and a curable silicone composition was produced as before. The organopolysiloxane shown in the formula below separated out onto the surface during curing of said curable silicone composition, and it was not possible to evaluate the physical properties of the material.



The curable silicone composition of the present invention is composed of component (A) and component (B). Component (A) is an organopolysiloxane composed of monofunctional siloxane units (M units) containing an organic group containing an epoxy group and quaternary functional siloxane units (Q units). The curing properties of the silicone composition are superior, and a hardened silicone material having superior flexibility and heat resistance after curing can be obtained.

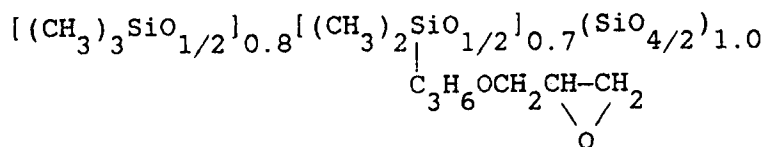
Claims

1. A curable silicone composition comprised of
(A) an organopolysiloxane represented by the formula

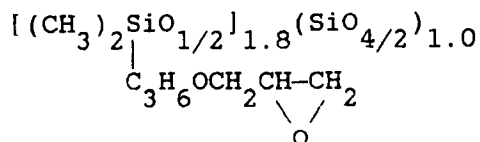


wherein R¹ is a monovalent hydrocarbon group except R¹ is not an alkenyl group; R² is a monovalent hydrocarbon group except R² is not an alkenyl group or hydrogen; R³ is selected from organic groups that contain an epoxy group or an alkoxysilylalkyl group with the proviso that at least one R³ group is an organic group containing an epoxy group; a is either 0 or a positive number; b is a positive number; c is a positive number; a/c has a value of between 0 to 4, b/c has a value of between 0.05 to 4, and (a + b)/c has a value of between 0.2 to 4; and (B) a curing compound selected from curing agents or curing catalysts.

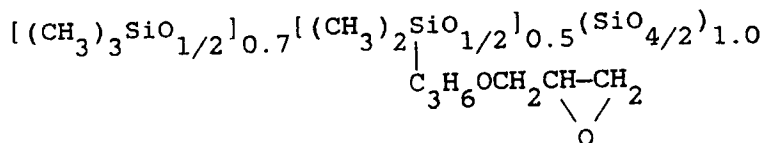
2. A composition as claimed in claim 1 wherein the curing agent (B) is selected from the group consisting of phenolic compounds, carboxylic acid compounds, acid anhydrides amine compounds, compounds containing alkoxy groups, mixtures thereof and partial reaction products thereof.
3. A composition as claimed in claim 1 wherein the curing catalyst (B) is selected from the group consisting of tertiary amine compounds, quaternary amine compounds, phosphorus compounds, aluminum compounds, and zirconium compounds.
4. A composition as claimed in claim 1 wherein there is 0.1 to 500 parts of (B) per 100 parts of (A).
5. A composition as claimed in claim 1 wherein there is additionally a filler.
6. A composition as claimed in claim 1 wherein there is additionally a ester based wax.
7. A composition as claimed in claim 1 wherein (B) is an organopolysiloxane represented by the formula



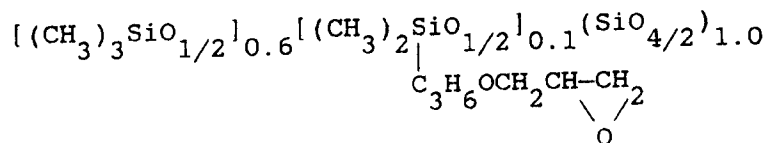
8. A composition as claimed in claim 1 wherein (B) is an organopolysiloxane represented by the formula



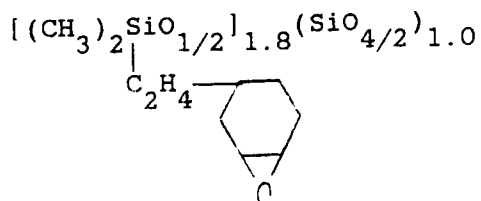
9. A composition as claimed in claim 1 wherein (B) is an organopolysiloxane represented by the formula



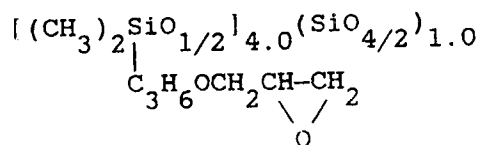
10. A composition as claimed in claim 1 wherein (B) is an organopolysiloxane represented by the formula



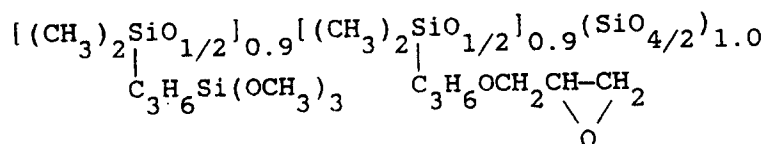
10 **11.** A composition as claimed in claim 1 wherein (B) is an organopolysiloxane represented by the formula



12. A composition as claimed in claim 1 wherein (B) is an organopolysiloxane represented by the formula



13. A composition as claimed in claim 1 wherein (B) is an organopolysiloxane represented by the formula



14. A composition produced by curing the composition as claimed in claim 1.



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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
E	DATABASE WPIL Week 9317, Derwent Publications Ltd., London, GB; AN 93-140390 & JP-A-5 078 450 (TOSHIBA SILICONE K.K.) 30 March 1993 * abstract *	1-6,8, 11,12,14	C08L83/06 C08L83/14 C08K5/00
P,X	& JP-A-5 078 450 (...)	1-6,8, 11,12,14	
X	GB-A-834 326 (MIDLAND SILICONES LIMITED) * claims * * example 4 * * page 2, line 72 - line 78 *	1-4,12 14	
Y	* page 2, line 105 - page 3, line 9 *	1-4,7-14	
P,Y	EP-A-0 541 988 (DOW CORNING TORAY SILICONE COMPANY, LIMITED) * claim 1 * * page 5, line 29 - line 36 * * examples *	1-4,7-14	
X	JOURNAL OF POLYMER SCIENCE, POLYMER CHEMISTRY EDITION vol. 28, no. 3, February 1990, NEW YORK US pages 479 - 503 , XP000141356 CRIVELLO ET AL. 'The Synthesis, Characterization, and Photoinitiated Cationic Polymerization of Silicon-Containing Epoxy Resins.' * page 481, paragraph 2 * * page 486, paragraph 3 * * page 503, conclusions * --- -/--	1,14	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C08L C08K C09D C09J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 JULY 1993	Examiner HOLLENDER C.J.F
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : number of the same patent family, corresponding document			



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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	POLYMER JOURNAL vol. 16, no. 6, 1984, TOKYO JP pages 495 - 504 CHUJO ET AL. 'Synthesis and Application of Polymerizable Silicone Oligomers from Water Glass.' * page 496, Method II, Scheme 1, Compounds 4b,5b * * Method II, pages 498-499 * ----	1,7-10	
A	EP-A-0 473 995 (GENERAL ELECTRIC COMPANY) * claims 1,2,5,8-10 * * page 4, line 8 - line 51 * ----	1,10	
A	GB-A-2 084 598 (GENERAL ELECTRIC COMPANY) * claim 1 * * page 4, line 5 - line 15 * -----	1,7-11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 JULY 1993	Examiner HOLLENDER C.J.F
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons ----- & : member of the same patent family, corresponding document			